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(54) Method of thermally treating and consolidating silica preforms for reducing laser-induced optical damage in silica

Verfahren zur thermischen Behandlung und zum Konsolidieren von Vorformen aus Siliciumdioxid zur Verminderung von durch Laser hervorgerufenen optischen Defekten

Procédé de traitement thermique et de consolidation de préformes en silice en vue de réduire les dommages optiques produits par l'application des lasers

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Description

[0001] This invention relates to a method for making a non-porous body of high purity fused silica glass whereby susceptibility to laser-induced optical damage is reduced by removal of oxygen. Specifically, the optical damage resistant silica of the invention is formed by consolidating a glass preform in a reducing atmosphere at high temperatures.

[0002] Although the exact origin, nature and mechanism of formation of the centers that give rise to absorptions in fused silica are not completely understood, these defects can be identified and tracked by optical absorption and/or electron spin resonance techniques. Two categories of defects can be described: the E' center, with an optical absorbance centered at about 210 nm and an oxygen related defect, having a very broad absorption band at about 260 nm with a corresponding fluorescence at 650 nm.

[0003] The E' defect structure consists of an electron trapped in a dangling silicon orbital projecting into interstitial space. As the E' center has an unpaired electron it is detectable by electron spin resonance spectroscopy.

[0004] Absorption spectra measured after prolonged exposure to 248 nm excimer laser show an extended absorption shoulder on the low energy side of a strongly peaked 210 nm absorption which extends beyond 260 nm. Unlike the 210 nm absorption band which is attributed to the Si E' center, the 260 nm absorption band is related to oxygen-related defects. A specific model put forth by Awazu and Kawazoe, J. Appl. Phys., Vol. 68, page 3584 (1990), suggests that the origin of the 260 nm absorption band is from the photolysis of dissolved molecular oxygen through a sequence of reactions.

[0005] One model for the formation of the 260 absorption involves the reaction of dissolved molecular oxygen with light to give oxygen atoms. The reactive oxygen atoms further react with molecular oxygen to give ozone (260 nm absorption). The ozone has a radiative transition with a red (650 nm) emission. Regardless of the mechanism of formation, it is important to note that the 260 nm absorption is related to the molecular oxygen content of the glass.

[0006] The dissolved molecular oxygen concentration of silica is dependent on the method by which the silica is made. For example, in a flame hydrolysis process, the dissolved molecular oxygen concentration depends on the CH_4/O_2 ratio in the flame used to synthesize SiO_2 from the silicon-containing compound. It has been found that the more oxidizing the flame used to make the glass, the more 260 nm absorption is produced with laser irradiation. Along with the 260 nm absorption is formed 1.9 eV (650 nm) red fluorescence. The 260 absorption is undesirable for KrF (248 nm) laser applications as the band is so broad that it encompasses the laser wavelength. Therefore, its minimization or elimination is important for the successful use of silica in KrF applications.

[0007] In the past, many methods have been suggested for improving the optical damage resistance of fused silica glass. For example, Faile, S. P., and Roy, D. M., Mechanism of Color Center Destruction in Hydrogen Impregnated Radiation Resistant Glasses, Materials Research Bull., Vol. 5, pp. 385-390, 1970, have suggested that hydrogen-impregnated glasses tend to resist gamma ray-induced radiation.

[0008] Japanese Patent specification 40-10228 discloses a process by which a quartz glass article made by melting, is heated at about 400 to 1000°C in an atmosphere containing hydrogen to prevent colorization due to the influence of ionizing radiation (solarization). Similarly, Japanese Patent specification 39-23850 discloses that the transmittance of UV light by silica glass can be improved by heat treating the glass in a hydrogen atmosphere at 950 to 1400 °C followed by heat treatment in an oxygen atmosphere at the same temperature range.

[0009] Shelby, J. E., Radiation effects in Hydrogen-impregnated vitreous silica, J. Applied Physics, Vol. 50, No. 5, pp. 3702-06 (1979), suggests that irradiation of hydrogen-impregnated vitreous silica suppresses the formation of optical defects, but that hydrogen impregnation also results in the formation of large quantities of bound hydroxyl and hydride, and also results in the expansion or decrease in density of the glass. It should be noted that all of these proposed methods involve treating silica in its consolidated form.

[0010] EP-A-0 483 752 relates to optical members made of synthetic silica glass which are resistant to high-power laser irradiation for long periods. The glass has hydrogen molecules in a concentration of more than 5×10^{16} molecules/cm^3, preferably more than 1×10^{17} molecules/cm^3 incorporated into internal regions thereof.

[0011] JP-A-60 090853 relates to a process whereby radiation resistance of quartz glass for optical fibers is improved by exposing the glass to a hydrogen containing atmosphere so that hydrogen is bonded to defects in the glass with introduction of hydroxyl groups.

[0012] WO-A-93 18420 relates to the production of reduced silica/germania glasses by subjecting the glass to a non-oxidising atmosphere, for example helium, preferably while the glass is in a porous state or in the form of a thin film. Reduced silica/germania glass is more sensitive to radiation in the band 225-275 nm and thus particularly adapted to making reflection gratings.

[0013] Our studies have shown that although the procedures described above diminish the absorption induced at 260 nm, the degree of improvement is inadequate for some applications of silica. Thus, there continues to be a need for new and improved methods of making high purity silica resistant to optical damage associated with prolonged exposure to 248 nm excimer laser. Accordingly, it is the object of the present invention to disclose a method of producing high purity fused

silica glass in which UV irradiation does not produce induced absorption at wavelengths close to 248 nm or fluorescence at 650 nm.

[0014] The present invention provides a method of making a non-porous body of high purity fused silica glass by the steps of:

a) producing a gas stream containing a silicon-containing compound in vapor form capable of being converted through thermal decomposition with oxidation or flame hydrolysis to SiO_2;
b) passing the gas stream into the flame of a combustion burner to form amorphous particles of fused SiO_2;
c) depositing the amorphous particles onto a support; and
d) consolidating the deposit of amorphous particles into a non-porous transparent glass body;
characterised in that consolidation takes place in a reducing atmosphere such that the particles are deoxygenated to the degree required to equate the oxygen chemical potential in the particles to that in the atmosphere.

[0015] The optical members produced have high resistance to induced absorption at 260 nm and induced fluorescence at 650 nm.

[0016] Optionally, after depositing the amorphous particles onto a support, the fused silica soot is exposed to a stream of chlorine gas to remove water from the silica.

[0017] Preferably the temperature of the reducing atmosphere during consolidation is in the range of 1000 to 1420°C.

[0018] As used in the present specification:

"260 nm absorption band" refers to the extended absorption shoulder on the low energy side of the strongly peaked 210 nm absorption generally found in the absorption spectra of fused silica glass;
"reducing atmosphere" refers to a gaseous atmosphere in which the chemical potential of oxygen is very low. Such an atmosphere tends to extract oxygen from any system in contact with it. Examples of reducing gases include hydrogen, carbon monoxide, diborane, and hydrazine vapor;
"forming gas" is used herein to refer to a He/H_2 mixture, one example of a highly reducing atmosphere employed during the consolidation of porous silica.

[0019] Reference is made herein to the drawings in which:

FIGS. 1(a) through 1(c) are comparative drawings of fused silica of the prior art after prolonged exposure to excimer laser, showing in particular, the extended absorption shoulder on the low energy side of the strongly peaked 210 nm absorption.
FIG. 2 is a graph of the absorption spectra of the inventive high purity fused silica of the invention after exposure to excimer laser of from 1 to 8 million pulses.
FIG. 3 is a graph comparing the absorbance at the 260 nm absorption band, of fused silica glass of the invention, one sample consolidated in forming gas, i.e. H_2/He, the other consolidated in CO, against a conventional fused silica glass consolidated in pure He, and a glass sample having an abnormally high level of oxygen.
FIG. 4 is an enlarged diagram of the spectral region around the 260 nm absorption band of FIG. 3, showing the absence of the extended absorption shoulder on the low energy side of the 210 nm absorption band in the inventive fused silica consolidated in a hydrogen/helium forming gas.

[0020] The invention will now be described with particular reference to the drawings. Until now, most high purity fused silica glass and glass members, when subjected to prolonged exposure to 248 nm excimer laser, exhibit an extended absorption shoulder on the low energy side of the strongly peaked 210 nm absorption. This extended absorption shoulder is being referred to herein as the 260 nm absorption band. Representative examples of absorption spectra showing the 260 nm absorption band for conventional fused silica are shown in FIGS. 1(a) to 1(c) respectively for glass after 1 to 4 million pulses at 350 mJ/cm^2. The fused silica of FIG. 1(a) was not annealed, while the glasses of FIGS. 1(b) and 1(c) were annealed at 1100 °C for 230 hours, and 1400 °C for 2 hours, respectively.

[0021] The 260 nm absorption band may result from the following sequence of equations:

$$O_2 + h\nu = 2O. \quad (1)$$

$$O_2 + O. = O_3(\text{ozone}) \quad (2)$$

$$O_3 + h\nu = O(^1D) + O_2 \quad (3)$$

$$O(^1D) = O(^3P) + 1.9\text{eV(red fluorescence)} \quad (4)$$

specifically, from equation (3) which is the photo decomposition of ozone. The subsequent return to the ground state of the oxygen atom in turn gives rise to the characteristic red fluorescence. Also, we have observed that the onset of absorption at 260 nm is always accompanied by the appearance and strength of the red fluorescence. The strength of the fluorescence scales with the strength of the absorption at 260 nm, indicating that they originate from the same process in agreement with the equations shown above.

[0022] The object of the present invention, that is, the production of glass in which 260 nm absorption and 650 nm fluorescence is not caused by exposure to laser radiation, is achieved by forming high purity fused silica glass by consolidating amorphous particles of fused sil-

ica in a strongly reducing atmosphere to remove molecular O_2 from the resulting silica. If the reducing atmosphere includes H_2, the hydrogen can rapidly diffuse into the silica where it may promote the reaction:

$$2H_2 + O_2 = 2H_2O \quad (5)$$

[0023] The concentration of H_2 in the forming gas is limited in order to minimize the potential formation of Si-OH, as measured by the value of the beta-OH. This formation of Si-OH may be the result of further reaction of the H_2O produced by equation (5) above with selected sites in the network, thus:

$$Si - O - Si + H_2O = 2Si - OH \quad (6)$$

Without intending to be bound by theory, this formation of Si-OH may also be the result of a competing reaction of the H_2 with the network in which case it is possible that not only Si-OH , but also Si-H is formed through the following equation:

$$Si - O - Si\ H_2 = Si - OH + Si - H \quad (7)$$

[0024] Therefore, if H_2 is employed, the amount H_2 in the He/H_2 forming gas mixture is limited by the above concern, and is best determined by experimentation for each given process.

[0025] According to the present invention, an optical member having high resistance to laser damage is formed by consolidating amorphous silica particles in a reducing atmosphere such as a hydrogen-containing atmosphere at a high temperature to make the glass resistant to laser damage.

[0026] If the reducing atmosphere comprises hydrogen, preferably the amount of H_2 is in the range of 0.1 to 10% of the total gas mixture. In one preferred embodiment, the amorphous particles are consolidated in a 95He/5H_2 atmosphere at a temperature in the range of 1000 to 1420°C.

[0027] This process wherein silica in the form of soot is exposed to a reducing atmosphere prior to and throughout the consolidation process differs significantly from earlier suggestions of hydrogen treatment. As mentioned above, several workers have suggested that the deleterious effects can be diminished by impregnating the glass with molecular hydrogen. Each has suggested that hydrogen reacts with the oxygen to produce water or hydroxyl groups. It should be noted, however, that this approach does not remove the oxygen from the glass; it merely incorporates it into another chemical compound. Therefore, it cannot be guaranteed that, under some conditions, irradiation will not be able to produce some of the same excited oxygen species responsible for the induced absorption and fluorescence.

[0028] The present invention has the advantage that it removes oxygen from the system completely instead of simply tying it up in a new chemical compound. The present invention comprises the steps of forming silica soot, subjecting the soot to an atmosphere of very low oxygen chemical potential (very strongly reducing), and subsequently consolidating the soot to form transparent glass. The process optionally may include a step in which the soot is dried by bathing it in a chlorine atmosphere prior to being exposed to the atmosphere of low oxygen chemical potential.

[0029] In the soot form, the particles of silica are small enough so that oxygen can diffuse a distance equal to the particle diameter in a number of seconds. Therefore, diffusion under the driving force of a gradient in the chemical potential can quickly deplete the silica of oxygen. The soot particles are deoxygenated to the degree required to equate the oxygen chemical potential in the silica to that in the atmosphere. After the glass has been consolidated, it is no longer influenced by the atmosphere because the path length across which oxygen can diffuse in reasonable times is minute compared to the size of the glass objects to be made from the consolidated silica. This is especially true when the temperature is lowered to values below the consolidation temperature.

[0030] The low chemical potential atmosphere can be achieved by utilization of any reducing gas at temperatures at or slightly below the consolidation temperature of the soot. Hydrogen, especially in the form of forming gas as described herein, and carbon monoxide are preferred gases because they are relatively inexpensive. As mentioned earlier, if hydrogen is used to control the chemical potential of oxygen in the atmosphere, some of the hydrogen may permeate the soot and react with oxygen to form some water. This is disadvantageous for applications in which low water or hydroxyl levels are required or desired. Therefore, for such applications our most preferred embodiment is the use of carbon monoxide.

EXAMPLE 1

[0031] To illustrate the efficacy of the present invention we have measured the 260 nm absorption and the 650 nm fluorescence induced by laser irradiation in four different glasses. Sample 1 was deliberately made under conditions such that it contained a higher than normal concentration of molecular oxygen. It is estimated that the glass contains about 5 x 10^{17} molecules of oxygen/cm^3. Sample 2 was made under standard (conventional) conditions. Sample 3 was consolidated in the presence of forming gas (H_2/He) in order to deplete the glass of oxygen. Sample 4 was consolidated in the presence of carbon monoxide. The object of this experiment was to demonstrate that the mechanism of oxygen removal was not a reaction with hydrogen, but rather diffusion, driven by the low chemical potential of oxygen in the reducing atmosphere. The absorbance at 260 nm induced by one million pulses of 193 nm irradi-

ation at a fluence of 65 mJ/cm^2 in each of the samples is shown in Table 1 below.

Table 1

Sample	1	2	3	4
Absorbance (cm^{-1})	0.3	0.05	0.02	0

[0032] Red fluorescence was observed in the standard sample (Sample 2), and very strong fluorescence was observed in the high oxygen sample (Sample 1). No red fluorescence was detected in either of the samples consolidated under reducing conditions. The sample consolidated under carbon monoxide exhibited no induced absorption whatsoever at 260 nm after one million pulses.

[0033] The absorption spectra of the high purity fused silica of the invention after exposure to 1 to 8 million pulses at 350 mJ/cm^2, and 400 Hz, are shown in FIG. 2. As can be seen in this diagram, there is a complete absence of extended absorption shoulders on the low energy side of the strongly peaked 216 nm absorption (i.e., the 260 nm absorption bands) that are present in FIGS. 1(a) to 1(c).

[0034] FIG. 3, is direct quantitative diagram comparing the absorbance at 260 nm, of two fused silica glass samples of the invention (1) consolidated in a H_2/He forming gas, and (2) consolidated in CO, against (3) a conventional fused silica glass consolidated in pure He, and (4) Sample 1 (glass containing abnormally high level of molecular oxygen). All four glass samples were irradiated with 193 nm excimer laser, at 63 mJ/cm^2, and 300 Hz. For the high oxygen fused silica, the extended absorption shoulders on the low energy side of the 210 nm absorption band are clearly visible immediately the sample is irradiated with the laser. No absorbance was observed for either the forming gas or Coconsolidated samples of the invention. For the conventional glass sample (3), consolidated under standard (prior art) conditions, after about thirty minutes, absorbance is observed in the 260 nm region, with the absorbance increasing with time. This is in sharp contrast, with the fused silica of the invention, for example, as shown in FIG. 2, where even after 8 million pulses, no extended bands were observed in the spectra in the 260 nm band region.

[0035] FIG. 4 is an enlarged diagram of the spectral region around the low energy side of the 216 nm absorption band of FIG. 3, comparing the spectrum of the conventional fused silica after 2 million pulses (line 1), against the spectrum of the inventive fused silica after 6 million pulses (line 2). The absorbance of the conventional fused silica in the 260 absorption band is 0.08/cm, while that of the inventive fused silica consolidated in forming gas is 0.03/cm.

EXAMPLE 2

[0036] In this example, a silica soot blank prepared by the outside vapor deposition process using octamethylcyclotetrasiloxane as the silica source was consolidated. The consolidation process was done by placing a piece of soot preform which was 7 mm in diameter and 13 mm in length into a quartz tube with a top equipped with gas ports. The quartz tube was then placed in a furnace at room temperature. The system was first purged with helium at 1000 °C for 15 minutes and then 4.32% hydrogen balance helium was flowed through the system at a rate of 1.5 liter per minute. The furnace temperature was raised to 1420 °C at a rate of 160 °C per hour maintaining the hydrogen/helium flow. The glass sample was cooled rapidly to 1000 °C again maintaining the hydrogen/helium flow. The sample was then cooled to room temperature in an air atmosphere.

EXAMPLE 3

[0037] This example was carried out again using a silica soot blank prepared by OVD using OMCTS as the silica source. The consolidation process was done by loading a piece of soot blank which was 7 mm in diameter and 11 mm in length into the quartz tube. The top of the tube was modified so that the gas flow was directed down the center of the blank. The tube was placed into a furnace at room temperature. The system was purged with helium at 1000 °C for 15 minutes and then 4.32% hydrogen balance helium was flowed through the system at a rate of 3 liter/minute. The furnace was ramped from room temperature to 1000 °C at a rate of 250 °C per hour. It was then held at 1000 °C for 2 hours. At the end of the two hour hold, the temperature was ramped to 1420 °C at a rate of 100 °C per hour. The glass sample was cooled to 200 °C over a 16 hour period continuing to flow hydrogen/helium. The glass was cooled from 200 °C to room temperature over a period of 4 hours under helium.

[0038] Useful silicon-containing compounds for forming the glass of the invention are known such as disclosed collectively in U.S. Patent No. 3,393,454; 5,043,002; 5,152,819; and 5,154,744. Preferably the silicon-containing gaseous feedstock includes halide-free, silicon-containing compounds that can be oxidized by flame hydrolysis or pyrolysis, to produce transparent, high-purity silica glass articles. The production of fused silica glass through the use of pyrolyzable and/or hydrolyzable halide-free, silicon-containing compounds as the feedstock components results in carbon dioxide and water as the by-products. Examples of useful halide-free silicon-containing compounds include cyclosiloxane compounds, preferably, polymethylsiloxane such as hexamethyldisiloxane, polymethycyclosiloxane, and mixtures of these. Examples of particularly useful polymethylcyclosiloxane include octamethylcyclotetrasiloxane, decamethylcylcopentasiloxane, hexamethylcy-

clotrisiloxane, and mixtures of these.

[0039] In addition to polymethylsiloxanes, organosilicon materials satisfying the following three criteria can also be used in the method of the invention:

(1) an operable organosilicon-R compound (R is an element of the Periodic Table) will have a Si-R bond dissociation energy that is no higher than that of the Si-O bond;
(2) an operable organosilicon-R compound will exhibit a significant vapor pressure at temperatures below 250° C and a boiling point no higher than 350° C; and, in the interest of safety,
(3) an operable organosilicon-R compound will, upon pyrolysis and/or hydrolysis, yield decomposition products besides SiO_2 which are deemed to be environmentally safe or the emissions are below acceptable governmental standards.

[0040] Three groups of compounds which have been found to be especially useful are categorized below according to the bonding arrangement in the basic structure:

(1) organosilicon-oxygen compounds, having a basic Si-O-Si structure, in particular linear siloxanes wherein an oxygen atom and a single element or group of elements, such as a methyl group, is bonded to the silicon atom;
(2) organosilicon-nitrogen compounds, having a basic Si-N-Si structure, such as aminosilanes, linear silazanes, and cyclosilazanes, wherein a nitrogen atom and a single element or group of elements are bonded to the silicon atom; and
(3) siloxasilazanes, having a basic Si-N-Si-O-Si structure, wherein a nitrogen atom and an oxygen atom are bonded to the silicon atom.

[0041] Other useful halide-free silicon-containing compounds for the method of the invention include octamethyltrisiloxane (an operable linear siloxane), aminosilanes such as tris (trimethylsilyl) ketenimine, linear silazanes such as nonamethyltrisilazane, cyclosilazanes such octamethylcyclotetrasilazane, and siloxasilazanes such as hexamethylcyclotrisiloxazane.

[0042] In one particularly useful method of the invention, halide-free, cyclosiloxane compound such as octamethylcyclotetrasiloxane (OMCTS), represented by the chemical formula, ---$[SiO(CH_3)_2]_4$---, is used as the feedstock for the fused silica boule process, or in the vapor deposition processes such as used in making high purity fused silica for optical waveguide applications.

[0043] In addition to halide-free cyclosiloxane compounds, $SiCl_4$ can also be used as the feedstock in the silica boule process to produce high purity fused silica of the invention. However, for safety and environmental reasons, halide-free, cylcosiloxane compounds are preferred.

Claims

1. A method for making a non-porous body of high purity fused silica glass by the steps of:

    a) producing a gas stream containing a silicon-containing compound in vapor form capable of being converted through thermal decomposition with oxidation or flame hydrolysis to SiO_2;
    b) passing the gas stream into the flame of a combustion burner to form amorphous particles of fused SiO_2;
    c) depositing the amorphous particles onto a support; and
    d) consolidating the deposit of amorphous particles into a non-porous transparent glass body;
    characterised in that consolidation takes place in a reducing atmosphere such that the particles are de-oxygenated to the degree required to equate the oxygen chemical potential in the particles to that in the atmosphere.

2. A method according to claim 1, wherein the temperature of the reducing atmosphere during consolidation is 1000 to 1420°C.

3. A method according to claim 1 or 2, wherein the reducing atmosphere comprises at least one of hydrogen, carbon monoxide, diborane and hydrazine.

4. A method according to claim 1 or 2, wherein the reducing atmosphere comprises carbon monoxide.

5. A method according to any of claims 1 to 4, wherein the silicon-containing compound comprises a halide-free polymethylsiloxane.

6. A method according to claim 5, wherein the polymethylsiloxane is hexamethyldisiloxane, polymethylcyclosiloxane, or a mixture thereof.

7. A method according to claim 6, wherein the polymethylcyclosiloxane is octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane, hexamethylcyclotrisiloxane, or a mixture thereof.

Patentansprüche

1. Verfahren zur Herstellung eines nicht-porösen Körpers aus Quarzglas hoher Reinheit durch folgende Schritte:

    a) Herstellung eines Gasstroms, der eine siliziumhaltige Verbindung in Dampfform enthält,

die durch thermische Zersetzung und Oxidation oder durch Flammenhydrolyse in SiO_2 umgewandelt werden kann;

b) Überführung des Gasstroms in die Flamme eines Verbrennungsofens, um amorphe Teilchen aus Quarzglas zu bilden;

c) Ablagerung der amorphen Teilchen auf einen Träger und

d) Konsolidierung der Ablagerung amorpher Teilchen zu einem nicht-porösen, transparenten Glaskörper;
dadurch gekennzeichnet,
daß die Konsolidierung in einer reduzierenden Atmosphäre stattfindet, so daß den Teilchen der Sauerstoff soweit entzogen wird, wie nötig ist, um das chemische Potential des Sauerstoffes in den Teilchen dem in der Atmosphäre anzugleichen.

2. Verfahren nach Anspruch 1, wobei die Temperatur der reduzierenden Atmosphäre während der Konsolidierung 1.000 bis 1.420 Grad Celsius beträgt.

3. Verfahren nach Anspruch 1 oder 2, wobei die reduzierende Atmosphäre zumindest eine der Verbindungen Wasserstoff, Kohlenmonoxid, Diboran und Hydrazin enthält.

4. Verfahren nach Anspruch 1 oder 2, wobei die reduzierende Atmosphäre Kohlenmonoxid enthält.

5. Verfahren nach einem der Ansprüche 1 bis 4, wobei die siliziumhaltige Verbindung ein halogenidfreies Polymethylsiloxan enthält.

6. Verfahren nach Anspruch 5, wobei das Polymethylsiloxan Hexamethyldisiloxan, Polymethylcyclosiloxan oder eine Mischung hiervon ist.

7. Verfahren nach Anspruch 6, wobei das Polymethylcyclosiloxan Octamethylcyclotetrasiloxan, Decamethylcylcopentasiloxan, Hexamethylcyclotrisiloxan oder eine Mischung hiervon ist.

Revendications

1. Un procédé de formation d'un corps non poreux en verre de silice fondue de haute pureté par les opérations consistant :

a) à produire un courant gazeux contenant un composé contenant du silicium sous forme de vapeur se prêtant à être transformé en silice par décomposition thermique avec oxydation ou hydrolyse à la flamme ;

b) à faire passer le courant gazeux dans la flamme d'un brûleur à combustion pour former des particules amorphes de silice fondue ;

c) à déposer les particules amorphes sur un support ; et

d) à consolider le dépôt de particules amorphes en un corps en verre transparent non poreux,
caractérisé en ce que la consolidation a lieu dans une atmosphère réductrice de telle manière que les particules se trouvent désoxygénées au degré voulu pour rendre le potentiel chimique de l'oxygène présent dans les particules égal à celui de l'atmosphère.

2. Un procédé selon la revendication 1, dans lequel la température de l'atmosphère réductrice pendant la consolidation est de 1000 à 1420 °C.

3. Un procédé selon la revendication 1 ou 2, dans lequel l'atmosphère réductrice comprend au moins un membre du groupe formé par l'hydrogène, le monoxyde de carbone, le diborane et l'hydrazine.

4. Un procédé selon la revendication 1 ou 2, dans lequel l'atmosphère réductrice comprend du monoxyde de carbone.

5. Un procédé selon l'une quelconque des revendications 1 à 4, dans lequel le composé contenant du silicium comprend un polyméthylsiloxane non halogéné.

6. Un procédé selon la revendication 5, dans lequel le polyméthylsiloxane est l'hexaméthyldisiloxane, un polyméthylcyclosiloxane ou un mélange de ces composés.

7. Un procédé selon la revendication 6, dans lequel le polyméthylcyclosiloxane est l'octaméthylcyclotétrasiloxane, le décaméthylcyclopentasiloxane, l'hexaméthylcyclotrisiloxane ou un mélange de ces composés.

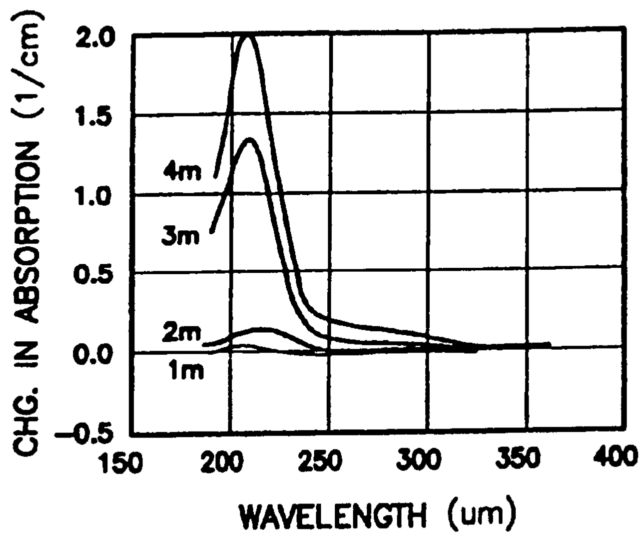

FIG. 1 (a)

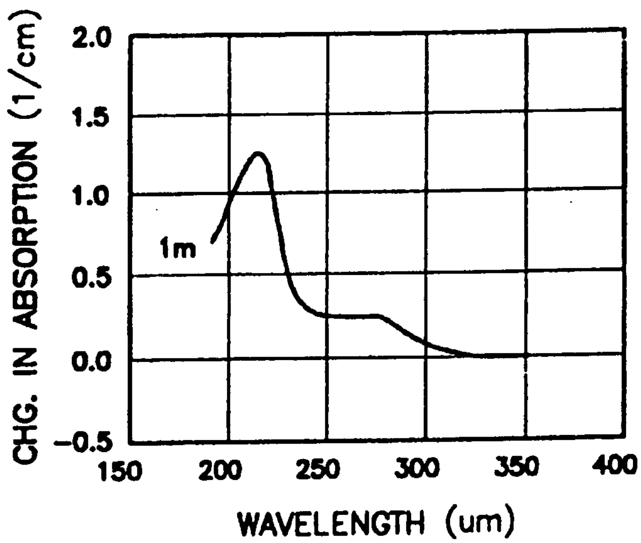

FIG. 1 (b)

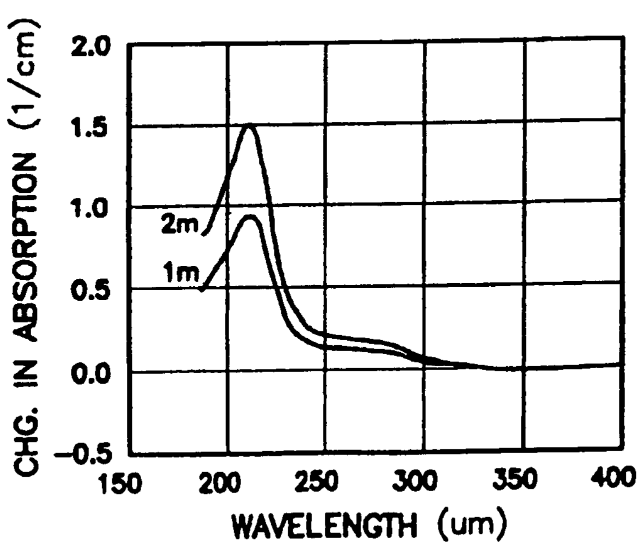

FIG. 1 (c)

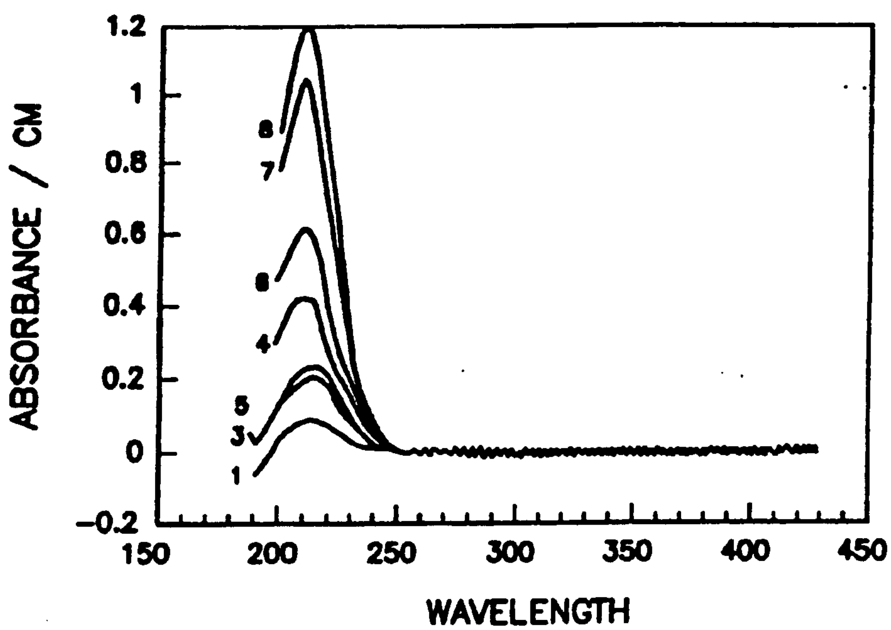
1.2
1
0.8
0.6
0.4
0.2
0
-0.2
ABSORBANCE / CM
150
200
250
300
350
400
450
WAVELENGTH
8
7
6
4
5
3
1

FIG. 2

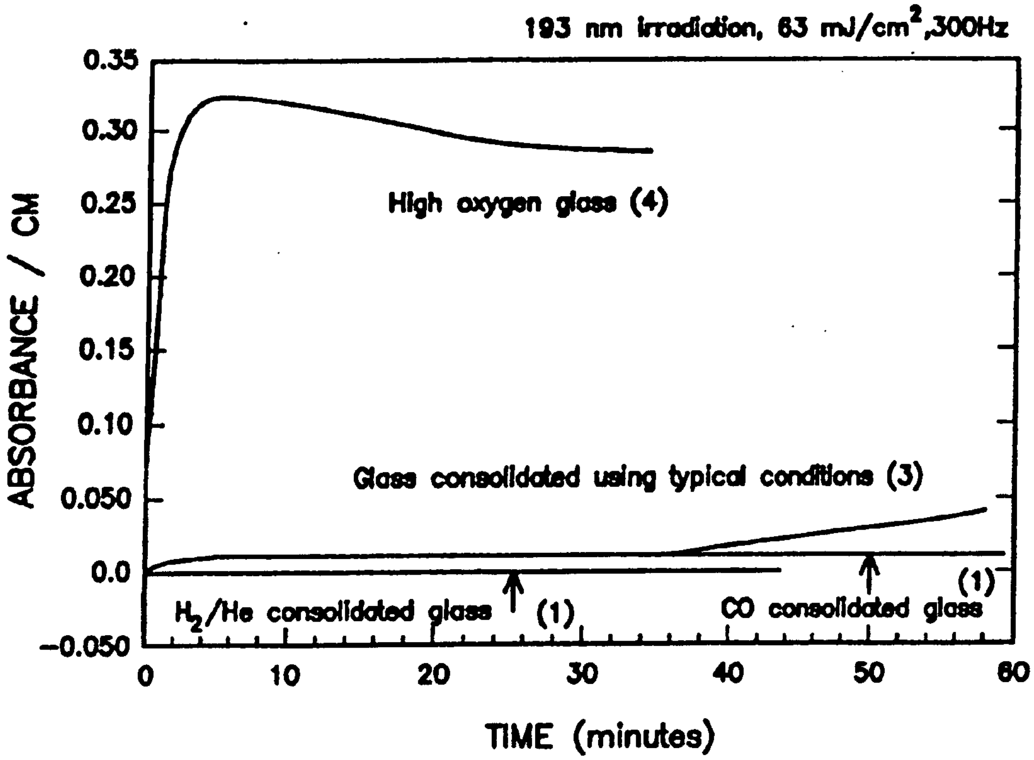
193 nm irradiation, 63 mJ/cm²,300Hz
0.35
0.30
0.25
0.20
0.15
0.10
0.050
0.0
−0.050
ABSORBANCE / CM
High oxygen glass (4)
Glass consolidated using typical conditions (3)
H₂/He consolidated glass
(1)
(1)
CO consolidated glass
0
10
20
30
40
50
60
TIME (minutes)

FIG. 3

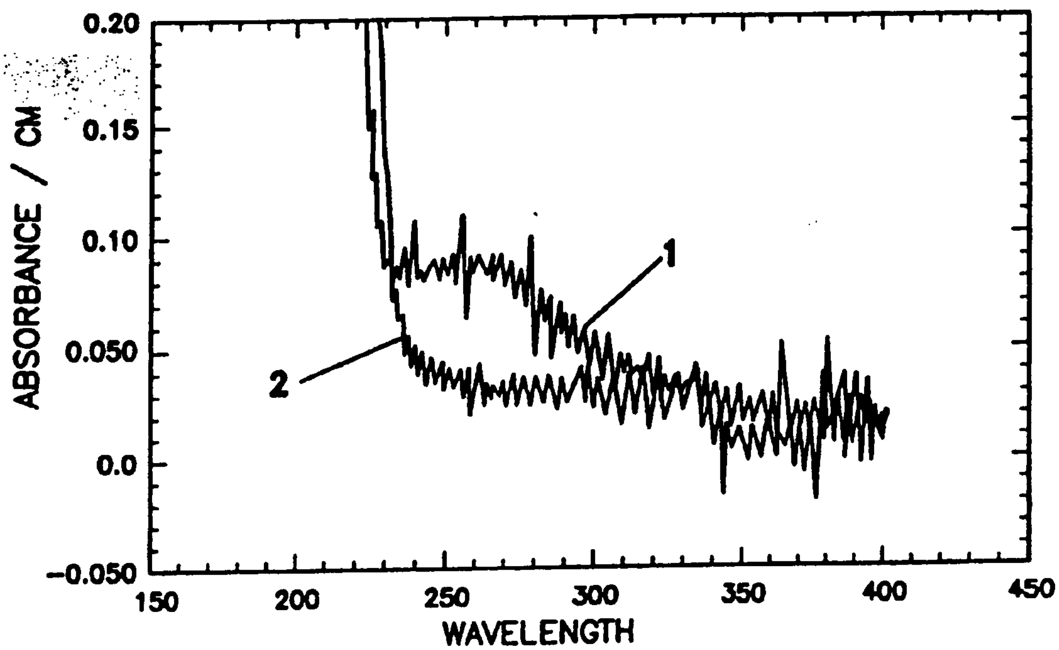
0.20
0.15
0.10
0.050
0.0
−0.050
ABSORBANCE / CM
150
200
250
300
350
400
450
WAVELENGTH
1
2

FIG. 4